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Photosensitization of TiO_2 by $[Fe^{II}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})_2(CN)_2]$: Band Selective Electron Injection from Ultra-Short-Lived Excited States

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The development of an inexpensive dye sensitized solar cell exhibiting a light-to-electrical conversion efficiency of 10% has brought the sensitization of large band gap semiconductor oxides to the forefront of photoelectrochemical research.[1] However, the recent technological advances have eclipsed the more fundamentally significant finding that extraordinarily high photon-to-electron conversion is being achieved with a transition-metal complex that has very poor photophysics in solution. The emitting state of the sensitizing dye $[Ru^{II}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})_2(NCS)_2]$ has a luminescence quantum yield of only 0.4% (125 K) and a 50 ns lifetime (298 K), rendering the complex unsuitable for solution photochemistry.[1] Yet the quantum yield for injection of an electron from the photoexcited dye into the TiO_2 conduction band is near unity,[1,2] and injection is reported to occur within *femtoseconds*.[2,3] These findings belie previous models of photochemical reactivity from transition metal bipyridyl complexes, which assume that long-lived excited states are beneficial and that photochemistry occurs only from vibrationally relaxed, lowest energy electronically excited states. We report here a novel, iron-based photosensitizer and suggest that photosensitization is occurring via an ultra-short-lived, upper excited state. It is the first efficient use of an iron bipyridyl complex in a photoconversion scheme, and our results significantly broaden the field of dyes that one might consider as photosensitizers. The dye also exhibits a unique "band selective" sensitization, effectively sensitizing TiO_2 from only one of its two absorbance bands.

Herein we report the sensitization of nanocrystalline TiO_2 by *cis*-$[Fe^{II}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})_2(CN)_2]$, a chromophore with an extremely short-lived, nonemissive excited state. The complex (inset, Figure 1) was prepared via a modified procedure of Schilt.[4] Its absorbance spectrum, shown in Figure 1, exhibits one bipyridyl based $\pi-\pi^*$ transition (318 nm) and two metal-to-ligand charge transfer (MLCT) bands (430 nm, 635 nm with a shoulder at ~550 nm). The complex adsorbs out of a 10^{-3} M methanolic solution containing 20 mM chenodeoxycholic acid[5] onto nanocrystalline films of TiO_2,[6] rendering the films a dark blue. Under white light illumination of approximately "one sun" (75 mW/cm^2, $\lambda > 400$ nm) in a regenerative cell configuration, a short-circuit photocurrent of 290 μA/cm^2 and an open circuit photovoltage of −360 mV are obtained (Figure 2). No attempt to optimize the cell performance was made.

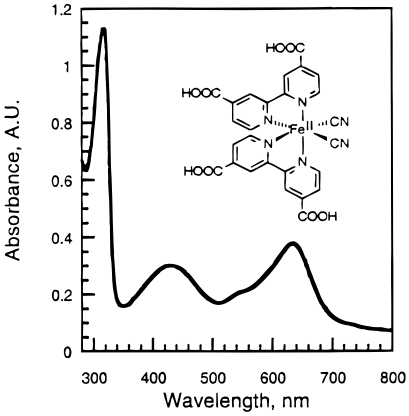

Figure 1. Absorption spectrum of $[Fe^{II}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})_2(CN)_2]$, structure shown in the inset, in dimethyl sulfoxide (8×10^{-5} M in a 1 cm path length cell).

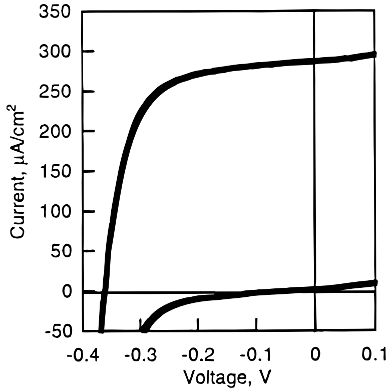

Figure 2. Current−voltage curve under white light illumination (upper curve) and in the dark (lower curve) of $[Fe^{II}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})_2(CN)_2]$ on TiO_2. The counter electrode is platinum and the electrolyte solution is 0.5 M LiI, 0.05 M I_2, 0.2 M 4-*tert*-butylpyridine in 9/1 (v/v) acetonitrile:3-methyl-2-oxazolidinone.

This is the first report of a substantial photosensitization effect by an iron(II) bipyridyl complex. Like those of bipyridyl complexes of ruthenium(II), their intense visible absorptions are due to excitation into initially singlet metal-to-ligand charge transfer (^{1}MLCT) states via $t_{2g} \rightarrow \pi^*$ electronic transitions. However, iron's weaker ligand field places the metal-centered antibonding e_g orbitals *lower* in energy than the ligand π^* orbitals. As a consequence, unlike ruthenium complexes, for which a ^{3}MLCT state is populated via intersystem crossing and persists for nano- to microseconds, iron complexes crossover to a ligand field (LF) state. There is a concurrent and substantial loss of excited state energy: for the tris-substituted complexes, the LF state is only 0.9 eV above the ground state.[7]

The LF state of the noncarboxylated analogue $[Fe^{II}(2,2'\text{-bipyridine})_2(CN)_2]$ has a 330 ps lifetime; its appearance is instantaneous after excitation into the MLCT band, within the

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[4] Schilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000−3005. A solution of 840.0 mg (3.44 mmol) of 2,2′-bipyridine-4,4′-dicarboxylic acid and 10 drops of 1 M NaOH in 40 mL of water was warmed; 451.0 mg (1.15 mmol) of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was added. Dropwise addition of 1 M NaOH was continued until complete dissolution of the ligand and subsequent formation of $[Fe^{II}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})_3][SO_4]$ was indicated by a clear, dark red solution. The solution was diluted to 70 mL and heated to 90 °C, and 868.0 mg NaCN were added. Heating was continued for 5 min. The pH of the cooled solution was lowered to 4.6, and the precipitated ligand was collected. The pH of the filtrate was further lowered to 2.5; the product $[Fe^{II}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})_2(CN)_2]$ was collected and rinsed with dilute H_2SO_4 and acetone. The complex (600 mg, 88%) was chromatographed on silica gel and recrystallized from methanol by addition of acetone.

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25 ps resolution of a transient absorption experiment.[8] However, it is unlikely that electron injection occurs from an LF state. In addition to there being significantly less driving force for injection, there is also a large reorganizational barrier to reaction since population of antibonding orbitals significantly lengthens the Fe−N bond;[7] furthermore, there is no direct orbital overlap between the iron-centered e_g orbitals and the acceptor orbitals in the TiO_2 conduction band. The band selectivity described below also strongly suggests that injection is occurring from the MLCT states, *before* the internal conversion event. Although [Fe^{II}(2,2′-bipyridine-4,4′-dicarboxylic acid)$_2$(CN)$_2$] would be predicted to have a longer lived LF state than [Fe^{II}(2,2′-bipyridine)$_2$(CN)$_2$], it would be predicted to have an even shorter lived MLCT state.[7,8] Therefore, assuming that adsorption does not alter the photophysics, injection must be occurring in less than 25 ps.[9] Reports in the literature for the time scale of electron injection from excited-state dyes bound to TiO_2 using time-resolved spectroscopy vary from nanoseconds[10] to femtoseconds.[2,3] However, kinetic measurements are made only on the dyed film, i.e., one neither contacting electrolyte nor connected in circuit to a counter electrode. Herein is supporting data for injection kinetics near the subpicosecond regime obtained in unambiguous, steady-state experiments in working cells without the use of a complicated laser spectroscopy apparatus.

Figure 3 shows the photocurrent action spectrum for [Fe^{II}(2,2′-bipyridine-4,4′-dicarboxylic acid)$_2$(CN)$_2$] on TiO_2 superimposed upon the absorption spectrum of the adsorbed dye. It can be seen that while injection is relatively efficient (10−11%) from the higher energy MLCT (∼420 nm), injection is much less efficient (∼2%) from the lower energy MLCT transition (∼600 nm). For all dyes heretofore reported in the literature, the photocurrent action spectra qualitatively trace the dyes' absorbance features. To our knowledge, this is the first observation of a "band selective" sensitization phenomenon. A precise explanation for why injection is more efficient from one of two absorption transitions is not yet possible without detailed knowledge of the excited-state configuration of [Fe^{II}(2,2-bipyridine-4,4′-dicarboxylic acid)$_2$(CN)$_2$].[11]

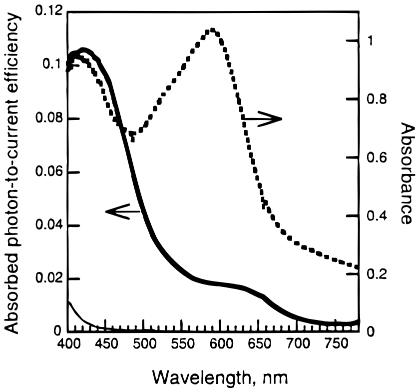

Figure 3. (---) Absorbance spectrum of [Fe^{II}(2,2′-bipyridine-4,4′-dicarboxylic acid)$_2$(CN)$_2$] adsorbed on TiO_2 in 0.5 M LiI in acetonitrile, obtained by subtraction of immersed TiO_2 film absorbance from immersed dyed film. (upper solid line) Photocurrent action spectrum of the same film; conditions as for Figure 2. Also shown (lower solid line) is the action spectrum of an undyed TiO_2 film.

Recent work by McCusker et al. indicates that vibrational relaxation, internal conversion, and intersystem crossing evolve simultaneously in ruthenium trisbipyridine and not via discrete and discernible transitions between states.[12] They suggest that initially excited states might in fact be accessible to photoconversion processes, and our results support this suggestion. We further demonstrate that dye-semiconductor systems can employ sensitizers whose photophysics otherwise limit their use in bimolecular quenching reactions. In conclusion, and on a practical note, the cost of iron is less than 1% of the cost of ruthenium. If iron-based complexes can be optimized to be efficient sensitizers, the overall cost of the already economical dye sensitized solar cell could be even further reduced.[13]

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Supporting Information Available: Electrochemical and spectroscopic analyses and estimated excited-state energetics of compound (1 page). See any current masthead page for ordering and Internet access instructions.

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